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NAVAL POSTGRADUATE SCHOOL Monterey, California



THESIS

DETERMINATION OF BULK MECHANICAL PROPERTIES OF
NANOSTRUCTURES FROM MOLECULAR DYNAMIC SIMULATION

by

Richard A. Duff

June 2003

Thesis Co-Advisors:

Young W. Kwon

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**DETERMINATION OF BULK MECHANICAL PROPERTIES OF NANO
STRUCTURES FROM MOLECULAR DYNAMIC SIMULATION**

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Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

from the

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ABSTRACT

Determining mechanical properties from microscopic forces has become important in the light of utilizing nano-scale systems. The molecular dynamics model was used to determine the modulus of elasticity and shear modulus of pure metallic micro lattice structures. Preliminary results indicate that the moduli of elasticity is determined to within 15% accuracy for 5 different metals of 500-atom structures when compared to the experiment values of bulk materials. Furthermore, the elastic modulus for copper structures was computed with different temperatures, different magnitudes of stresses and various kinds of dislocations. From the preliminary results, it is concluded that the model accurately determines the mechanical properties of the nano-scale systems.

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LIST OF SYMBOLS

a_i	Molecular (or Atomic) acceleration
\mathbf{e}	Strain
\mathbf{z}	Strength of Interaction
e	Electron Charge
E	Modulus of Elasticity
E_{ee}	Embedding Energy
E_{gs}	Ground State Energy
E_H	Energy of Host
E_{kin}	Kinetic Energy
E_{pot}	Potential Energy
E_{tot}	Total Energy
E_{sys}	System Energy
f	Force of Interaction
F	Intermolecular Force
F_{ija}	Force Between Atoms in the \mathbf{a} -Direction
$F_h[\mathbf{r}_h(r)]$	Functional of the Host Electron Density
\mathbf{f}_{ij}	Short Range Pair Interaction
$\mathbf{j}(r_{ij})$	Short Range Electrostatic Pair Potential
G	Shear Modulus
\hat{H}	Hamiltonian
J_{ab}	Components of the Global Stress Tensor
k	Boltzman Constant
l	Length due to Tensile Stress
l_0	Original Length With no Tensile Stress
m	Atomic mass
M	Number of Time Origins
$\mathbf{h}(t)$	Auto-correlation of the Global Stress Tensor
$n(r)$	Number Density
N	Number of Atoms
p_i	Momentum of Atom i
\mathbf{r}	Electron Number Density
\mathbf{r}_h	Host Electron Density
$\mathbf{r}_{h,i}$	Host Electron Density as Seen by Atom i
\mathbf{r}_N	Atom Number Density
r_{ij}	Distance Between Atoms i and j

r_{ijb}	Distance Between Atoms in the <i>b</i> -Direction
r_c	Interaction Cutoff Range
<i>t</i>	Length Scale
<i>S</i>	Tensile Stress
<i>S</i> _{<i>ii</i>}	Atomic Stress Tensor Component
<i>t</i>	Time Step (for Autocorrelation)
<i>t</i> ₀	Initial Time
<i>t</i> _{<i>n</i>}	Time at Time Step <i>n</i>
<i>T</i>	Temperature
<i>u</i>	Lennard-Jones Potential Energy or Pair Potential
<i>U</i>	Intermolecular Potential Energy
<i>g</i>	Poisson Ratio
<i>v</i>	Velocity
<i>v</i> _{<i>x</i>}	Component of Velocity in the x-Direction
<i>v</i> _{<i>y</i>}	Component of Velocity in the y-Direction
<i>v</i> _{<i>z</i>}	Component of Velocity in the z-Direction
<i>v</i> _{<i>ia</i>}	Velocity of Atom <i>i</i> in the <i>a</i> -Direction
<i>v</i> _{<i>ib</i>}	Velocity of Atom <i>i</i> in the <i>b</i> -Direction
<i>Vol</i>	Volume
<i>V</i> (<i>r</i>)	Potential Function
<i>x</i> _{<i>i</i>}	Position of Atom <i>i</i>
<i>y</i>	Wave Function
<i>Z</i>	Atomic Number

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I. INTRODUCTION

A. OBJECTIVES

As technology advances, there are ever-increasing demands to place more and more technological advances into the same volume. This volume limitation is especially true for systems that operate in unfriendly environments, for example space. A shuttle that operates in space is limited by its carrying capacity. Equipment that is necessary for monitoring shuttle systems currently is typically hard mounted on surfaces and takes up precious bulkhead area. As technology develops, there is an ever-increasing pressure to miniaturize such instruments, and perhaps embed them into the structure. A key issue is whether the structure can retain its material properties and not be weakened by the embedded device. Carbon nanotube materials have shown excellent properties such as elasto-mechanical and both semi-conducting or metallic, depending on their configuration.[1] Properties which give carbon nanotubes excellent prospects for embedded nano-scale sensors. Carbon nanotubes have also shown that they can be formed into various components from the nano-transistor to nano-mechanisms, such as pumps and containment devices[2]. Embedding carbon nanotube structures and sensors would be beneficial in reducing the real estate costs normally associated with carrying externally mounted devices. This thesis is a provisional investigation into the mechanical properties of nano-scale systems embedded in bulk materials. We examine the link between microscopic and macroscopic behaviors of such materials. Specifically, this thesis will study the modulus of elasticity(E) and

shear modulus(G) that can be obtained from molecular dynamic simulations using microscopic principles.

B. BACKGROUND

Predicting the physical properties of macroscopic systems from the microscopic nature of their constituent atom is a difficult problem. Yet the problem is one that must be addressed if we are to develop useful technologies based on embedded nano-scale sensors. Traditionally there have been two ways of tackling this kind of problem. The first is a first principles, "brute force" method using quantum mechanics. This method is severely constrained by the size of the system it can handle. A truly first-principles approach in predicting the behavior of systems where quantum effects are significant, is prohibitively costly in terms of computing power. The second method is molecular dynamics, which solves the problem by making specific assumptions from the onset to simplify the problem[3].

In this thesis we will see that a combination of techniques borrowed from molecular dynamics and quantum mechanics can be used to model nano-structures. Both molecular dynamics and quantum mechanics will be discussed separately below, followed by a discussion on how they merge.

1. Molecular Dynamics

In almost all cases, molecular dynamics simulations are based on the Lennard-Jones potential of inter-atomic

interactions. For a pair of atoms i and j located at \vec{r}_i and \vec{r}_j the potential energy is given by [4]:

$$u(r_{ij}) = 4\mathbf{z} \left[\left(\frac{\mathbf{t}}{r_{ij}} \right)^{12} - \left(\frac{\mathbf{t}}{r_{ij}} \right)^6 \right],$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r = |\vec{r}|$ and \mathbf{z} and \mathbf{t} are phenomenological parameters specific to each material system. The Lennard-Jones potential features a short-range repulsive potential together with a long-range attractive potential. The $1/r^6$ attractive potential arises from fluctuating dipole moments on neutral atoms, while the $1/r^{12}$ term models the short-range repulsion that arises from the Pauli exclusion effects of overlapping electron clouds. The Lennard-Jones potential defines the repulsion, attraction and finally the cutoff range where the potential no longer is applicable. The first simplification in molecular dynamics is to ignore the attractive tail. The above equation can be modified to:

$$u(r_{ij}) = 4\mathbf{z} \left[\left(\frac{\mathbf{t}}{r_{ij}} \right)^{12} - \left(\frac{\mathbf{t}}{r_{ij}} \right)^6 \right] + \mathbf{z}, \quad r_{ij} \leq r_c = 2^{1/6} \mathbf{t},$$

with r_c chosen such that $u(r_c) = 0$. What we want is the force of the interaction that is given by $\vec{f} = -\nabla u(r)$, which results in:

$$\vec{f}_{ij} = \frac{48\mathbf{z}}{\mathbf{t}^2} \left[\left(\frac{\mathbf{t}}{r_{ij}} \right)^{14} - \frac{1}{2} \left(\frac{\mathbf{t}}{r_{ij}} \right)^8 \right] \vec{r}_{ij}.$$

As r increases to r_c the force drops to zero, which prevents any discontinuities.

So far only a two-atom system has been discussed. For an N -atom system, the total intermolecular potential

function is represented by $U(r^N)$. Relating this to our Lennard-Jones pair potential $u(r_{ij})$ we have [5]:

$$U(r^N) = \sum_j \sum_{i < j} u(r_{ij}) .$$

Since, at the micro-scale, there are no dissipative forces acting among molecules, intermolecular forces are conservative and the total force acting on molecule i is:

$$\vec{F}_i = - \frac{\partial U(\vec{r}^N)}{\partial \vec{r}_i} ,$$

which is equivalent to:

$$\vec{F}_i = m \vec{a}_i .$$

Therefore the kinetic and potential energies, per atom, can be written as:

$$E_{kin} = \frac{1}{2N} m \sum_{i=1}^N v_i^2 ; \text{ and}$$

$$E_{pot} = \frac{4z}{N} \sum_{1 \leq i < j \leq N} \left(\frac{t}{r_{ij}} \right)^{12} - \left(\frac{t}{r_{ij}} \right)^6 ,$$

where $E_{tot} = E_{kin} + E_{pot}$ as usual.

Molecular dynamics simulations compute the motions of individual molecules. From this motion, molecular dynamics simulation has direct access to the energy and pressure of a system in equilibrium. Energy and pressure can be expressed in terms of temperature and density. It is the measurements of the temperature and density of a system, using molecular dynamics, which provides access to the thermodynamics of a system and it is the thermodynamics of a system that give us a detailed description of the microscopic behavior.

If we turn this around and specify the position of the atoms of a system, the energy can be determined. This

scheme is called the embedded atom method (EAM)[6]. Daw [7] also showed that the energy of a system of atoms is uniquely specified by the its electron density. From the system energy, by using numerical methods, the forces can be determined as well as the thermodynamic properties of the material. The embedded atom method is one schemes used in order to obtain system energies. The energy of a system can be represented again by [8]:

$$E_{tot} = E_{kin} + E_{pot} ; \text{ or}$$

$$E_{tot} = \sum_i E_{ee}(\mathbf{r}_{h,i}) + \frac{1}{2} \sum_{i,j} \mathbf{f}_{ij}(r_{ij}),$$

where $\mathbf{r}_{h,i}$ is the total electron density seen by atom i due to the rest of the atoms in the system, E_{ee} is the embedding energy for placing an atom into that electron density and \mathbf{f}_{ij} is the short range pair interaction representing the core-core repulsion of atoms i and j separated by distance r_{ij} . Quantum mechanic provides a means of obtaining these quantities.

2. Quantum Mechanics

In this section, only highlights of the important parts will be discussed.

In a perfect world, the exact solution for the time independent Schrodinger equation for an N-electron wave function could be determined. However determining the exact solution is complex if not "hopeless"[9]. Basically the problem is to solve the Schrodinger wave equation in

its time dependant form for a particle of energy moving in a potential V in three dimensions[10]:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V\Psi(x,y,z,t)=i\hbar\frac{\partial\Psi}{\partial t},$$

where $\Psi(x,y,z)$ is the wave function for N atoms and potential V could be a function of space and time. Using variational (Hartree-Fock method) calculations of self-consistent fields, one can narrow down a solution. By incorporating the Slater determinant, one can identify a solution that includes the requirements of the Pauli exclusion pricipal. A direct, frontal assault on the many electron Shrodinger equation is impractical for systems containing more than a few electrons. We are guided, however, in developing approximate methods by the Ritz variational principle, which says[11]:

$$E_{gs} \leq \frac{\langle \mathbf{y} | \hat{H} | \mathbf{y} \rangle}{\langle \mathbf{y} | \mathbf{y} \rangle}$$

where \hat{H} is the Hamiltonian and is given by[12]:

$$\hat{H} = \sum_{i=1}^N \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{|r_i - r_j|}.$$

By taking into account the normalization[13]

$$\int d^3r |\mathbf{j}(r)|^2 = 1$$

and with some manipulation, we end up with the Hartree-Fock equations. The problem is that the Hartree-Fock method works for atoms with few electrons. Even with today's computers this method is cumbersome.

The Thomas-Fermi method, introduced in the 1920's, showed promise in evaluating the energy for atoms with many electrons. In this method the potential is expressed in

terms of the particle number density at a position vice the traditional probability density, as used above. For example[14]:

$$n(r) = \frac{1}{3\pi^2 \hbar^3} (-2mV(r))^{\frac{3}{2}}.$$

The above equation is a semi-classical approximation that assumes that there are many electrons within volume elements in which the potential is nearly constant and the wavelength is small since the electrons are assumed to be in a state of high energy[15]. The problem with the Thomas-Fermi method is that it is not very accurate for small ranges, since the potential changes become large. Also it is not very accurate for large ranges when the wavelength becomes large.

Density Functional Theory changes the form of the solution for which we are looking. Specifically, given a potential, the above solution results in an electron density, where the energy is a functional of that potential. Hohenberg and Kohn[16] stated that there existed a functional defined for all non-degenerate ground state densities such that, for a given potential, the quantity has its unique minimum for the correct ground state density, associated with the potential. In other words, the energy is a function of the density, and the potential can be determined by the electron density (to within a constant).

Next Stott and Zaremba[17][18] proved a useful corollary, in that the energy of an impurity in a host is a function of the function (or functional) of the electron density of that same host without impurities, or

$E_H = F_r[\mathbf{r}_h(r)]$, where $\mathbf{r}_h(r)$ is the pure host electron density.

From the corollary, the conclusion was drawn that the embedding energy of an impurity can be determined from the electron density of the host before the impurity is added. Daw and Baskes[19] then showed that the energy then is a function of the electron density at the site of the impurity plus an additional electrostatic interaction term. Mathematically:

$$E_{sys} = F_h(\mathbf{r}_h(r_i)) + \frac{1}{2} \sum_j \mathbf{j}(r_{ij}),$$

where \mathbf{r}_h is the electron density of the host without impurity, and \mathbf{j} is the short range electrostatic pair potential. The total energy of a system is the superposition of all contributions[20]:

$$E_{tot} = \sum_i F_h(\mathbf{r}_h(r_i)) + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \mathbf{j}(r_{ij})$$

3. Paradyn

Paradyn[21] is the computer code used in this thesis to solve numerically for the total energy of a metallic based system. From the code, thermodynamic properties are obtained that can be used for a variety of purposes. The properties required by this thesis are the global off diagonal stresses and the elongation length of a cubic metallic lattice, due to a tensile loading stress.

There are two main input files required to run Paradyn. The first file contains the embedded potential, and pair interaction information. The second file sets up the thermodynamics for determining the kinetic energy.

The potential file contains the following information: atomic number; atomic mass, lattice spacing, potential cutoff range for each atom, grid of inter-atomic force,

grid of atom electron density and the spherically averaged atomic density[22]. The grid of the atom electron density is interpolated for each atom site in order to determine the electron density at each atom. The inter-atomic force is also interpolated for each atom site and multiplied with the atom density in order to determine the embedding energy of each atom. The embedding energy is then summed over all the host atoms keeping to the predetermined cutoff range, in order to determine the cohesion energy of the system. Finally, the electron density at each atom is multiplied by the embedded energy, which determines the force on each atom. The components of the individual atomic force tensor, multiplied by the inverse of the corresponding neighbor range squared, are used to determine the stress tensor for each atom.

The thermodynamic file takes the temperature required by the user and computes the local velocity of each atom by $v = \sqrt{2Tk/m}$. In order to ensure the system represents a real model, random numbers are generated and assigned to the initial velocities, which are used to develop the overall velocity distribution, so that $v_x = v * \text{randomnumber}$. v_y and v_z are determined in the same fashion. The kinetic energy of each atom is determined from the three velocity components

$$E_{kin} = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2).$$

The individual kinetic energies are then

summed over all the atoms to determine the total kinetic energy of the system. The user using this file also inputs the number of atoms that define a system. The velocities are also used in determining the diagonal components of the stress tensor for each atom. For example: $\mathbf{s}_{xx} = m(v_x v_x)$. Once

the stress tensor is obtained the pressure of the system can be determined by:

$$P = (\mathbf{s}_{xx} + \mathbf{s}_{yy} + \mathbf{s}_{zz}) / 3Vol$$

With the stress tensor developed by both the kinetic energy and potential energy routines, the velocity of the kinetic energy routine is adjusted in an iterative loop until the temperatures of the two separate routines are within tolerance. Depending on the initial user flags, the tolerance can be dictated by the user. For the program details, refer to either the Paradyn computer code or supporting documentation.

4. Elastic Properties

In general the microscopic stress tensor is of the form:

$$J = \begin{bmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{bmatrix}$$

where J_{ab} measures the rate at which the **b**-directed momentum is transported in the **a**-direction[23]. The stress tensor components are made up of both kinetic and potential energy parts as shown below:

$$J_{ab} = m \sum_i v_{ia} v_{ib} + \frac{1}{2} \sum_{i \neq j} r_{ijb} F_{ija}$$

where the first term is equivalent to the kinetic energy and the second term the potential energy. For a homogenous isotropic material the stress tensor is symmetric. In

order to obtain the stress auto-correlation function, the off diagonals are used in the form:

$$\mathbf{h}(t) = \frac{\mathbf{r}_N}{3kT} \frac{1}{N} \sum \langle J_{ab}(t_0) J_{ab}(t_0 + t) \rangle$$

$J_{\alpha\beta}$ is the sum of two terms, thus the correlation function $\eta(t)$ has three contributions: (a) a kinetic term, which measures the correlation of the momentum transport caused by atomic motions; (b) a potential term, which measure the correlation of momentum transport cause by inter-atomic forces; and (c) a cross term which measures the coupling of atomic motions and forces.[24]

For programming purposes the above equation can be simplified to:

$$\mathbf{h}(t) = \frac{\mathbf{r}_N}{3kT} \frac{1}{NM} \sum \sum_n^M J_{ab}(t_n) J_{ab}(t_n + t)$$

where M is the number of samples. In the static limit as t goes to 0, the shear modulus $\mathbf{h}(0)$ can be obtained. This thesis compares the shear modulus obtained by microscopic means and compared to that obtained for macroscopic systems to ensure the modulus is preserved in some form or another.

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II RESULTS AND DISCUSSION

This section will outline the procedure used in the determination of the Modulus of Elasticity and the Shear Modulus from the data produced from multiple Paradyn simulations. The mechanical properties will then be directly compared to known values. Five substrate materials were selected for this baseline comparison. Specifically copper, nickel, gold, silver and platinum and monel. It should be noted that all references to the auto-correlation function refer to the C++ program at Appendix A.

A. MODULUS OF ELASTICITY

Initially Paradyn was run with no tensile load. The no load case provided a baseline of how the lattice structure equilibrated and subsequently vibrated. The vibrations are due to the kinetic energy of the individual atomic structures. Once the no load case data was obtained, the sample was subjected to a load of 10 MPa of tension. Again the sample increased in size and then oscillated. For this thesis the structure was allowed to increase to its equilibrated size, then oscillate through two full periods. In Figure 1, a sample of platinum was allowed to equilibrate at loads of 0 MPa and 10 MPa of tension. The initial expansion of the sample is evident. Once the initial expansion is over the sample can be seen to oscillate. In Figure 2, the oscillations over two full periods are expanded. The increase in separation of the

equilibrium length is what is critical in determining the elastic modulus.

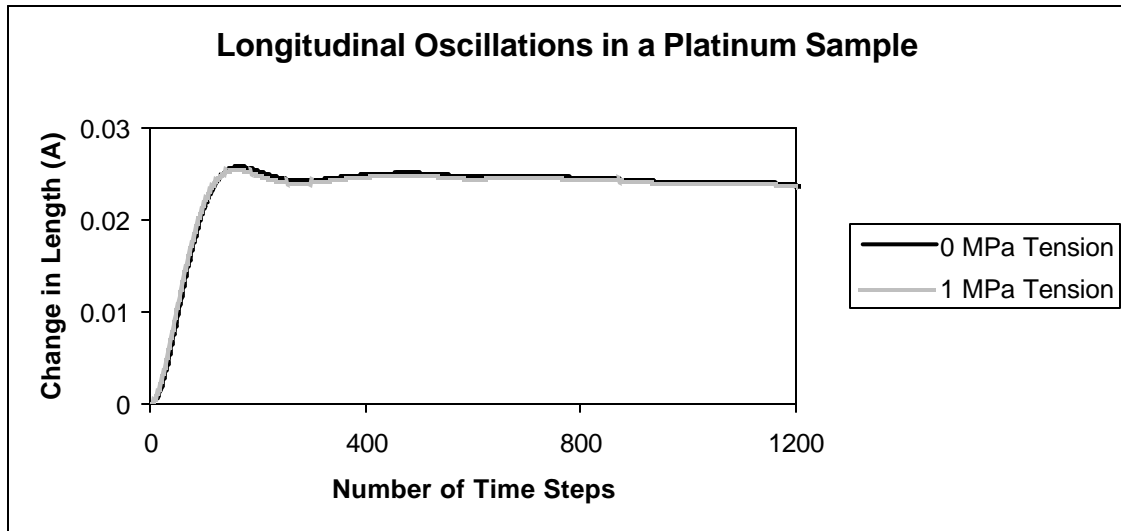


Figure 1. Longitudinal Changes in Length of a Platinum Sample With No Load and 10MPa of Tension. Temperature is 300K. One Time Step is 5 ps.

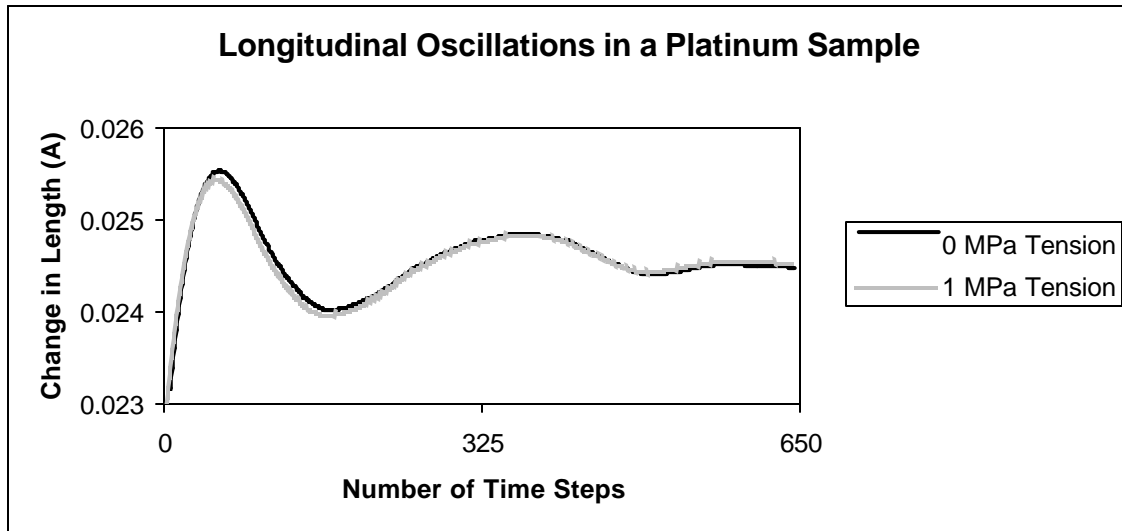


Figure 2. Expansion of Figure 1. The Longitudinal Changes in Length of a Platinum Sample With No Load and 10 MPa of Tension. Expansion Consists of the Re-centered Time Steps 110-540 From Figure 1, In Order to Encompass Two Full Periods of Oscillations.

In determining the elastic modulus, first the non-loaded sample was allowed to expand and come to equilibrium for a minimum of two complete oscillatory periods. The average amplitude of the period peaks was used to determine the mean length of the sample (l_0). Next a tensile stress (\mathbf{s}) was applied to the sample. Again the sample was allowed to expand and cycle through at least two full cycles. The mean length of the period peaks was used to determine the elongated length l . The strain (\mathbf{e}) was then determined by $\mathbf{e}=(l_0-l)/l_0$. The modulus of elasticity (E) was then calculated in the normal way by $E=\mathbf{s}/\mathbf{e}$. The modulus of elasticity determined from Paradyne is listed and compared in Table 1.

Sample	Modulus of Elasticity (GPa) Theoretical from Reference (25)	Modulus of Elasticity (GPa) Calculated from Paradyne
Ni	220.7	252.0
Monel	144.9	161.7
Pt	146.9	150.1
Cu	117.2	120.8
Au	74.48	80.70
Ag	72.41	75.45

Table 1. Comparison of the Theoretical and Calculated Modulus of Elasticity

A sample of the alloy monel was also tested. The sample of monel consisted of 64% nickel atoms and 33% copper atoms, where the copper atoms were placed in a nickel substrate at random. The result for monel is as expected. The modulus of elasticity was expected to be between the values obtained for pure samples of nickel and copper. From Table 1, the simulated moduli of elasticity are greater than the theoretical values. It is the difference in methodology between the techniques that plays

an important role. The modulli resulting from the simulations are based on pure metallic samples, whereas the theoretical values are based on bulk material test samples. These test samples are made of real materials that contain impurities and crystalline structures.

The copper sample was exposed to increasing temperatures and increasing tensile stresses. The results of the increasing temperature runs are found in Table 2 and the results of the increasing tensile stress are found in Figure 3.

Average Internal Temperature (K)	Modulus of Elasticity (GPa)
150	220.8
222	220.9
422	43
851	3

Table 2. Modulus of Elasticity as a Function of Temperature for a Sample of Pure Copper. Results are Based on Simulation and are within 15% of the theoretical value. The Melting Point of Copper is 1084.62 C [26]

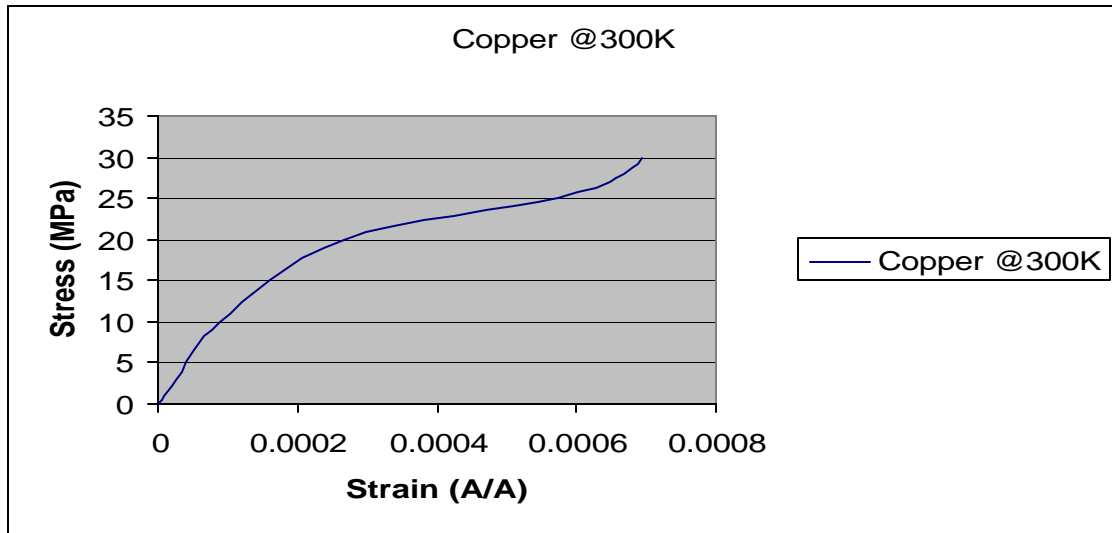


Figure 3. Stress Strain Curve of a Sample of Pure Copper. Data Obtained from Simulation. Theoretical Yield Strength of Copper is 27.5 MPa. [27]

Further analysis of the Elastic Modulus was completed using the same copper sample, in that dislocations were added to the sample. In the first run 10 copper atoms were removed at random, run 2 had 20 atoms randomly removed and finally a block of 28 atoms were removed from the center of the sample. The results of these runs are found in Table 3

Sample Description	Applied Tensile Stress (Bar)	Modulus of Elasticity (GPa)
500 Atom Sample	10	120.7
10 Random Atoms Removed	10	115.8
20 Random Atoms Removed	10	43
Core (Block of 28 Atoms) Removed	10	6

Table 3. Modulus of Elasticity for a Sample of Pure Copper with Dislocated Atoms. Temperature Constant at 300K, With an Applied Tensile Stress of 10 Bar.

For all the runs in which the Modulus of Elasticity was determined, the values were comparable to the

theoretical values. From at Table 1, where the six baseline substrates are directly compared, the modulus of elasticity for these six materials are not only in the correct order but they have values within 15% of their respective theoretical values.

Table 2 illustrates that as the temperature of the copper sample is increased, the modulus of elasticity decreases. This trend is correct and is one reason that many metal materials are worked at higher temperatures. It takes less energy to form the material at the higher temperature, because it is less stiff.

Figure 1 is the result of a plot of stress versus strain for the copper sample. The plot of the resulting Paradyn output data is representative of a typical Stress-Strain curve plot of a metallic material.

For the copper sample with dislocations, Table 3, illustrates that as atoms are removed the elastic modulus decreased as expected. Also, there is a difference in the modulus of elasticity in how the atoms were removed. For random atom removals, the modulus decreases gradually as more and more atoms are removed. For the removal of a block of atoms, the modulus decreases abruptly. Of note, the run data show that the atoms migrate towards the dislocations and take up new equilibrium positions as compared to the sample with no dislocations. As well, for the runs where 20 or more atoms were removed, the sample volume decreased overall. Although this decrease in volume is in the order of cubic angstroms, it was none the less present.

B. SHEAR MODULUS

As described earlier, molecular dynamic simulations typically compute the shear modulus by the virial expression:

$$\lim_{t \rightarrow 0} h(t) = \frac{\mathbf{r}_N}{3kT} \frac{1}{NM} \sum \sum_n^M J_{ab}(t_n) J_{ab}(t_n + t)$$

A C++ program was written in order to determine the shear modulus from the Paradyn stress output file. The code for this program is included at annex A.

The theoretical value of the shear modulus was determined by[28]:

$$G = \frac{E}{2(1+g)} ;$$

where E is the modulus of Elasticity and g is the material's Poisson ratio.

Table 4 contains the calculated theoretical shear modulus and the shear modulus computed from the stress auto-correlation function based on Paradyn output data.

Sample	Poisson Ratio [25] ¹ , [29] ² [30] ³	Theoretical Shear Modulus (GPa)	Experimental Shear Modulus (GPa)
Ni	0.31 ³	84.2	94.0
Pt	0.39 ¹	52.8	54.5
Cu	0.36 ²	43.1	59.0
Au	0.42 ¹	26.2	33.9
Ag	0.37 ¹	26.4	41.2

Table 4. The Theoretical Shear Modulus as Determined from the Modulus of Elasticity (given in Table 1) and the Poisson Ratio. The theoretical and experimental shear modulus' are presented side by side for direct comparison.

From Table 4, the resulting shear modulii computed from Paradyn data are representative of the theoretical

values. For nickel, platinum and copper, the values of the shear modulus agree to within 15%. For silver and gold the experimental shear modulus is off by approximately 30-50%

III CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

Bulk properties of materials in macroscopic systems are well defined and can easily be obtained from destructive testing of material samples. Computer simulations have also been successful at modeling these properties on a macroscopic scale. As technology advances to produce sensors and machines on a nano-scale, the task at hand is to determine the mechanical properties of these micro-systems so that when used they do not lose these properties and become a single point of failure in a critical system. Therefore it is important that a good model would combine Molecular Dynamics and Quantum Mechanics in order to determine the mechanical properties from interactions on an atomic level.

In this thesis the Paradyn model was used to determine the mechanical properties of pure metallic samples containing about 500 atoms. Preliminary analysis of the data from the Paradyn simulations is encouraging. The results show that, for the six substrate samples chosen, the modulus of elasticity can be obtained to within 15% of the theoretical value. In the simulations where the copper sample was exposed to increasing tensile stress, temperature and number of dislocations, the trend for the elastic modulus is reasonable. In plotting the stress and strain for a copper sample, the resulting stress strain curve was shown to be a typical representation of a metallic material. Finally, the simulation where atoms

were dislocated from the sample material illustrates that Paradyn was capable of producing results that were reasonable.

From the resulting data it can be concluded that Paradyn has the ability to simulate a micro-metallic system from which the bulk mechanical properties of the system are preserved. These results also indicate that the Paradyn model does accurately determine the inter-atomic forces between atoms of a metallic sample.

B. RECOMMENDATIONS

This thesis provides baseline material for obtaining mechanical properties of pure microscopic metallic systems using the Paradyn model of molecular dynamic simulation. In order to advance research into incorporating the embedding of micro technology to include carbon nanotube structures the following recommendations are made.

1. Conduct simulations for alloy and composite materials that could also be used as potential substrate materials;
2. Determine if the model accurately reflects material defects such as hydrogen embrittlement or atomic impurities.
3. Further research the determination of the shear modulus in order to determine if the model does accurately compute the microscopic stress tensor from the inter-atomic forces.
4. Conduct simulations where carbon nanotube structures are embedded into substrates.

APPENDIX A C++ CODE TO DETERMINE THE SHEAR MODULUS

```

//*****
//File: stress.cpp
//Name: Richard Duff
//PH0080 Thesis
//17 March 2003
//Description: This program calculates the modulus
// by using the off diagonal relaxation stresses
// from paradyn and solving the using autocorrelation
//*****
#include <stdio.h>
#include <math.h>
#include <stdlib.h>
//-----
//
// Initial values
//
//-----
const double boltz=8.62E-5, msteps=20.0, natoms=500.0;
const double temp=147.5784, vol=5452.596;
//-----
//
//Variables
//
//-----
int i, t;
float fa[25], fb[25], fc[25];
double ACF, etat, rho;

main()
{
    //Initialize setup parameters
    rho=natoms/vol;
    //Set up for file read and write
    FILE *fp;

    //read stress matrix
    fp=fopen("nnonpotstress.txt","r");
    for (i=0;i<20;++i)
    {
        fscanf(fp, "%E %E %E", &fa[i], &fb[i], &fc[i]);
    }
    fclose(fp);
}
```

```

// this loop is only for verification purposes to ensure
input is correct
    fp=fopen("ninonpotcopy.txt","w");
    fprintf(fp,"Input - The Off Diagonal Stress Tensor
Components Are:\n");
    fprintf(fp,"          J12                      J13
J23\n\n");
    for (i=0;i<20;++i)
    {
        fprintf(fp,"%14.5E      %14.5E      %14.5E\n", fa[i], fb[i],
        fc[i]);
    }
    fclose(fp);
    // Open file for output data
    fp=fopen("ninonpotmodulus.txt","w");
    printf("t          ACF");

    //loop for number of time origins
    fprintf(fp,"Nickel room temp not minimized using pot
file only");
    fprintf(fp,"\n      t          ACF
Eta(t)\n\n");
    for (t=0;t<20;++t)
    {
        // loop for number of sample points
        ACF=0.0;
        for (i=0;i<(20-t);++i)
        {

            ACF=ACF+(fa[i]*fa[i+t]+fb[i]*fb[i+t]+fc[i]*fc[i+t]);
        }
        ACF=ACF/(20);
        printf("%4d      %14.5E\n",t,ACF);
        etat=(rho*ACF)/(3*boltz*temp*natoms);
        fprintf(fp," %4d      %14.5E
%14.5E\n",t,ACF,etat);

    } //end t
    fclose(fp);
    return (0);

} //end main()

//end of file stress.cpp

```

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